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(54) High-surface-area compositions.

(57) Polyaromatic fibers or microbeads which are swollen with solvent and crosslinked while swollen in such a way that the expanded, or macronet, structure of the swollen fiber or microbead is stabilized and retained even after drying, exhibit high surface area and significant adsorptive capacity.

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Description

HIGH-SURFACE-AREA COMPOSITIONS

This invention relates to polymeric adsorbents and more particularly to high-surface-area polymeric fibers and microbeads useful as adsorbents.

Adsorbents are commonly solid materials which exhibit selectivity at their surface for substances in a mixture, thereby providing a means of separating such substances from the mixture. The high surface area characteristic of adsorbents (usually well above 5 m²/g of material) normally results from a fine particle size (non-porous adsorbents) or from pores in the adsorbent particles (porous adsorbents). Carbon black, TiO₂ and ZnO pigments are examples of non-porous adsorbents. Granular carbon, silica gel, bone char, certain soils and asbestos are examples of well-known porous adsorbents obtained from naturally occurring materials. These suffer seriously from high moisture adsorption in humid atmospheres, poor reproducibility during manufacture, and fragmentation during use in cyclic processes, because their rigid structures are broken by the high osmotic pressure of adsorbed materials in their small pores.

For separation or purification of complex substances (such as pharmaceuticals) synthetic adsorbents have been developed, some of which serve also as ion exchange materials or as intermediates for the manufacture of ion exchange materials. However, ion exchange is an absorption as well as an adsorption phenomenon, so that although all ion exchange materials are adsorbents, the converse is not necessarily true.

The synthetic adsorbents generally are porous polymeric solids, polystyrene and styrene-divinylbenzene copolymers being representative. Although it is possible to prepare synthetic polymers that are finely divided or to grind such polymers to a fine particle size, to obtain high surface area, fine particle size adsorbents cannot be used in cyclic processes, particularly processes involving columns, since the fine particles pack too tightly and impede flow. Moderately large adsorbent particles, from about 0.02 mm to 2 mm diameter or larger, are therefore required. Polymeric beads, obtained by known suspension polymerization techniques, have a convenient particle size for use in columnar operations. While the polymeric adsorbents can be made hydrophobic and the bead form makes them more useful, their adsorbent properties have been too limited for the adsorbents to compete effectively with the carbonaceous adsorbents obtained by pyrolyzing of organic materials.

Macronet adsorbents in bead form are described in US-A-4,263,407, which is hereby incorporated into the present specification by reference. They are produced by swelling a lightly crosslinked, macroreticular, aromatic polymer bead in an inert organic solvent, and then post-crosslinking the swollen beads with an external crosslinker. These adsorbents are called "macronets" because the crosslinks are stable and have a long and rigid structure which allows the polymer to retain the displacement of the chains to significant distances from one another that occurs during solvent swelling, even after the solvent has been removed. US-A-4,543,365 discloses similar bead materials, but employing more highly crosslinked resins.

DD-A-229,992 teaches a one-step preparation of high-surface-area, sulfonic acid resin beads from lightly crosslinked, suspension-polymerized polystyrene beads by chloromethylation and sulfonation in the presence of a swelling solvent; the resulting beads appear to be macronet beads.

Fibres have particular advantages over conventional adsorbents like carbon filaments or granular, activated carbons; they may be woven or otherwise processed into cloth or other textile materials for making garments protective against chemicals, filters for air purification systems, and the like. They, and other polymeric adsorbents, are also easier to regenerate and less sensitive to high humidity than activated carbons.

Fibers, by their small diameter, provide relatively high surface areas, and chemically modified, polystyrene-based fibers are known, as for example those of Yoshioka et al., Bull. Chem. Soc. Japan 56, 3726 (1983) or Japanese Kokai 77-120986. These fibers are composites of a vinylaromatic polymer matrix and longitudinal fibrils of alpha-olefin polymer imbedded in the matrix. The references teach treatment of the vinylaromatic surface of the fibers to attach functional groups such as sulfonic acid groups and amine or ammonium groups.

Japanese Kokai 75-145617 discloses treating phenol-formaldehyde polymer fibers with alkylating reagents such as paraformaldehyde in acidic media, a reaction which the above Yoshioka and Kokai 77-120986 use to prepare the surface for functionalization. In Kokai 75-145617 this reaction is followed by a mild pyrolysis in an oxidizing atmosphere at temperatures from 250 to 450°C; the reference reports that this treatment enhances the surface area of the fibers to at least 10 m²/g and as much as 400 m²/g.

Another approach to porous fibers is disclosed by Sruta et al., *Chemicke Vlakna*, 1986, 36, No. 3, pages 175-181. This reference discloses porous polyester fibers formed when calcium carbonate, spun into the fibers as a delustrant, is dissolved with acid.

We have discovered a process for increasing the surface area of crosslinked poly(vinylaromatic) polymers in the form of fibers or emulsion-polymerized particles, which process comprises swelling the polymer in a swelling agent which does not deactivate Friedel-Crafts catalysts and which does not interfere with the formation of a macronet structure, and subsequently introducing additional crosslinking into the polymer to stabilize its swollen structure.

The polymers which are converted to macronet structures in the process of the invention are poly(vinylaromatic) polymers, more preferably polystyrene, poly(alpha-methylstyrene) and polymers of styrene ring substituted by 1-3 alkyl groups of 1-3 carbon atoms each. Minor amounts, i.e. less than 50% by weight, of

other monoethylenically unsaturated monomers capable of copolymerizing with the aromatic monomer may be copolymerized with it. A particularly preferred polymer is a heterogeneous polymeric fiber comprising a matrix of the polyaromatic polymer described above, optionally blended with another polymer, preferably a polyolefin, and imbedded longitudinally therein filaments of a second polymer phase, the second polymer being preferably a polyolefin and more preferably polypropylene or polybutenes such as poly(butene-1) or poly(3-methyl-1-butene). The diameter of the imbedded filaments may range from about 1 to about 10 μm . The polymer may be formed into fibers using conventional processes such as the melt spinning process described by Yoshioka et al., Bull. Chem. Soc. Japan, Vol. 56, page 3726 (1983).

Another preferred polymer is an emulsion polymerized poly(vinylaromatic) polymer as described above, in the form of a particle in the diameter range from about 0.01 to about 1 μm . Such particles are referred to herein as microbeads, and may be prepared according to emulsion or latex polymerization procedures that are well known in the art, such as those of US-A-4,200,695. Forming the macronet structure in such particles increases their size significantly above the size of the original polymer particle.

Preferred swelling agents have a boiling point above about 50°C at atmospheric pressure, although lower boiling solvents may be used at higher pressures and temperatures above about 50°C. Suitable swelling agents which meet these criteria may readily be selected by one skilled in the art from among aromatic hydrocarbons, halogenated hydrocarbons, nitroparaffins, nitroaromatic compounds, ring-halogenated aromatic compounds, aliphatic hydrocarbons of about six or more carbon atoms, and carbon disulfide.

Also suitable but less preferred as swelling agents are aliphatic and aromatic ethers of five or more carbon atoms. Swelling agents which participate in the crosslinking reaction are contemplated within the scope of the invention, so long as they do not interfere with the reaction. Such participating swelling agents are at least difunctional, examples are aliphatic 1,2-dihalo materials and side-chain chlorinated dialkylaryl hydrocarbons. Mixtures of the useful swelling agents may also be used.

Examples of suitable swelling agents selected from the above groups include toluene, xylene, chlorobenzene, styrene monomer, ethylene dichloride, propylene dichloride and alpha, alpha-dichloro-p-xylene.

The stabilizing crosslinks, i.e., the long, rigid crosslinks that stabilize the expanded, or macronet, structure of the polymer, may either be formed by adding a crosslinking reagent to the swollen polymer, or by adding a crosslink-promoting catalyst to a swollen polymer which contains active crosslink sites.

The matrix polymer of the fibers and the emulsion polymer do not normally contain a significant number of active crosslinking sites unless a monomer containing active sites is employed, such as vinylbenzyl chloride, or unless it is treated further. A preferred treatment for introducing active crosslinking sites is haloalkylation. In this treatment a haloalkylating reagent such as methyl chloromethyl ether is allowed to react with the polymer to introduce haloalkyl groups which act as active crosslinking sites.

The catalysts useful for promoting the crosslinking reaction include the Friedel-Crafts catalysts, preferably Lewis acids such as ferric chloride, stannic chloride, aluminum trichloride, aluminum tribromide, boron trifluoride and zinc dichloride. The preferred Lewis acid is ferric chloride.

The catalyst, optionally as a solution, is allowed to contact the swollen polymer containing the active crosslinking sites, preferably at a temperature of from about 15°C to about 100°C, and allowed to react for from about two hours to about 24 hours at a temperature from about 15°C to about 150°C, preferably from about 85°C to about 105°C, to produce the macronet structures of the invention.

In the absence of active crosslinking sites, the swollen matrix polymer or the emulsion polymer may also be crosslinked to form the macronet fibers or microbeads of the present invention by reacting it with a crosslinking reagent, as mentioned above. The crosslinking reagent is an acylating or alkylating agent, which includes the haloalkylating reagents useful for introducing active sites. Other haloalkylating reagents may be used, such as alpha, alpha-dichloro-p-xylene, dichloromethane, bis(4,4'-chloromethyl) biphenyl, bis(chloromethyl)thiophene, 1,4-dichloro-hexane, 1,4-dichlorobutane, chloroform and carbon tetrachloride. Other alkylating reagents such as polyols and polyolefins may also be used, for example, alkylene glycols such as ethylene glycol and propylene glycol, diepoxides and polybutadienes. The alkylating agent may contain aromatic groups, provided the atoms of the alkylating agent which bond to the polymer are aliphatic carbon atoms. The alkylating agent may also be paraldehyde, formaldehyde or a formaldehyde generator in the presence of a strong acid such as sulfuric acid.

Difunctional acylating agents are also suitable for introducing active crosslinking sites; these agents are preferably aromatic, but may include aliphatic compounds. The preferred acylating agents are diacid chlorides, as for example fumaryl dichloride, maleyl dichloride, malonyl dichloride, oxalyl chloride, succinyl dichloride, adipyl dichloride and sebacyl dichloride. In the case of aromatic diacid chlorides the carbonyl groups must be separated by at least one carbon atom; suitable aromatic diacid chlorides include terephthaloyl chloride and isophthaloyl chloride, but not orthophthaloyl chloride (the carbonyl groups of which are not separated by at least one carbon atom) because it tends to form anthraquinone rings which in turn participate in redox reactions. Further suitable diacid chlorides include the 1,4-, 1,5- and 1,6-naphthoyl dichlorides and anthracene-1,5- and 1,9-diacid chlorides. Other suitable acylating agents include phosgene and thiophosgene. Other agents may act as crosslinkers, as for example sulfur halides such as sulfur monochloride, sulfur dichloride, and the corresponding sulfur bromides. The crosslinking reagent is allowed to react with the swollen polymer at a temperature of from about 15°C to about 150°C for from about two to about 24 hours.

Either process for forming the macronet crosslinks may occur in the presence of low-molecular weight

coupling agents such as alpha,alpha-dichloro-p-xylene, trivinylbenzene and terephthaloyl dichloride.

The macronet fibers and emulsion polymer particles of the invention possess a high surface area, as measured by nitrogen adsorption (BET). They have high adsorptive capacity for gases and vapors. They may be functionalized with chemically active functional groups to enhance selectivity of adsorbates, or to react with adsorbates. Examples of such groups include sulfonic acid groups, dimethylaminomethyl groups, quaternized alkyltrimethylammonium groups and oxime groups. They can provide an adsorptive filter medium which has the adsorption rate of a bed of fine particulate adsorbents while avoiding the problems of high pressure drop and filter clogging.

The following examples illustrate the invention. All proportions are by weight unless otherwise stated, and all reagents are of good commercial quality unless otherwise stated.

EXAMPLE 1

This example illustrates the preparation of the preferred, non-homogeneous, polypropylene-in-polystyrene polymer and fibers from that polymer. This preparation is described in the Yoshioka reference cited above, and is believed to be the procedure by which the fiber samples used in the following examples were prepared; the actual fiber samples were obtained from Toray Industries, Sonoyama, Otsu 520, Japan.

Sixteen polypropylene filaments are melt spun at 255°C within a matrix fiber of polystyrene blended with 20% by weight polypropylene; the weight ratio of polypropylene filaments to matrix polymer is 1:1. The fiber is drawn to five times its original length, to form a fiber 24 μ m in diameter and containing 16 filaments of polypropylene, each 4.2 μ m in diameter, embedded within the polystyrene-polypropylene matrix.

A portion of the resulting fibers is lightly crosslinked using a solution of 5% by weight paraformaldehyde, 25% by weight glacial acetic acid and 70% by weight concentrated sulfuric acid; a second portion is highly crosslinked using a similar reagent, and a third portion is uncrosslinked.

The three samples of fiber prepared according to the procedure above were tested for surface area by BET (using a Quantasorb Surface Area Analyzer and dried samples), and for elemental analysis; the following results were obtained:

Fiber Sample	Crosslinking	Surface Area (m ² /g)	Elemental Analysis (%)			
			C	H	O	Cl
A	None	< 1	88.17	10.95	--	--
B	Light	< 1	86.31	10.71	1.47	--
C	High	< 1	87.71	10.61	0.08	--

EXAMPLE 2

This example illustrates chloromethylation of the fibers of Example 1 to produce fibers having active crosslinking sites. For each of the crosslinked, heterogeneous fibers of Example 1, a 10 g sample was added to 80 ml methyl chloromethyl ether at ambient temperature, and the mixture was stirred for one hour. A solution of 9.4 ml stannic chloride in 10 ml methyl chloromethyl ether was added to the mixture over a period of 15 minutes while maintaining the temperature at 25-30°C, the low temperature being selected to minimize secondary crosslinking. When the addition was complete the mixture was held at 30°C for 4.5 hours, then cooled to 20°C, and 125 ml water was added over a period of 30 minutes while maintaining the temperature below 35°C, to quench the reaction. The solution was stirred for an additional 30 minutes, the fibers were filtered, and a wash step of resuspending in 100 ml deionized water, stirring for 30 minutes and refiltering was repeated twice. The fibers were then air dried for one hour and dried in a vacuum oven overnight at 50-60°C. This procedure yielded 19.1 g of chloromethylated fiber containing 66.9% solids. Elemental analysis of the fiber showed 73.0% carbon, 8.96% hydrogen and 17.3% chlorine. The surface area of the chloromethylated fiber, measured by BET, was less than 1 m²/g.

EXAMPLE 3

This example illustrates forming a macronet fiber from the chloromethylated fiber of Example 2. A 0.67 g sample of the fiber from Example 2 was transferred to a 100 ml, 3-neck flask fitted with reflux condenser and magnetic stirrer; 50 ml ethylene dichloride were added and the mixture was stirred for two hours to swell the polymer. To the mixture 0.5 ml stannic chloride was added, and the mixture was heated to reflux and allowed to reflux for 16 hours. The mixture was allowed to cool to room temperature, and the reaction was quenched by adding 100 ml acetone. The acetone was decanted from the fibers, which were washed once with another 100

ml of acetone and twice with 100 ml portions of water, the wash liquid being decanted from the fibers after each wash. The fibers were filtered and then allowed to air dry for one hour. The air-dried fibers were dried under vacuum at 50 -60°C overnight.

EXAMPLES 4-24

The procedure of Example 3 was repeated, varying the starting fiber, the type and amount of the Friedel-Crafts catalyst and the solvent. Stannic chloride, aluminum chloride and ferric chloride were employed at mole ratios of fiber to catalyst ranging from 1.1:1 to 3.7:1, and solvents used were ethylene dichloride or dichloromethane; in Examples 13 and 14, 3.7 millimoles para-dichloroxylenes was also present.

The fibers used were prepared according to Example 1, except that initial crosslinking of the fiber was either high or low. The resulting macronet fibers were examined for appearance and tested for surface area by BET; the results for these examples are shown in Table 1.

TABLE I

Sample from Example No.	Polymer Crosslinking (mmol)	Catalyst (mmol)	Ratio*	Solvent	Fiber Appearance	Surface Area by BET m ² /g
3	High(5.8)	SnCl ₄ (4.3)	1.3	EDC	Good	247
4	Low(5.8)	SnCl ₄ (4.3)	1.3	EDC	Good	172
5	High(12.5)	SnCl ₄ (8.5)	1.5	EDC	Good	246
6	Low(12.5)	SnCl ₄ (8.5)	1.5	EDC	Good	186
7	High(9.6)	AlCl ₃ (8.6)	1.1	EDC	Poor	--
8	Low(9.6)	AlCl ₃ (8.6)	1.1	EDC	Poor/Good	339
9	High(9.6)	AlCl ₃ (3.5)	2.7	EDC	--	311
10	Low(9.6)	AlCl ₃ (3.5)	2.7	EDC	Good	< 10
11	High(9.6)	SnCl ₄ (6.4)	1.5	MC	Good	< 10
12	Low(9.6)	SnCl ₄ (6.4)	1.5	MC	Good	< 10
13	High(9.6)	SnCl ₄ (6.4)	1.5	EDC**	Excellent	194
14	Low(9.6)	SnCl ₄ (6.4)	1.5	EDC**	Good	183
15	High(25.5)	SnCl ₄ (17.1)	1.5	MC	Good	< 10
16	Low(25.5)	SnCl ₄ (17.1)	1.5	MC	Good	< 10
17	High(25.8)	SnCl ₄ (17.1)	1.5	EDC	Excellent	304
18	Low(25.8)	SnCl ₄ (17.1)	1.5	EDC	Good	283
19	High(25.5)	AlCl ₃ (13.9)	1.8	EDC	Poor	426
20	Low(25.5)	AlCl ₃ (13.9)	1.8	EDC	Poor	586
21	High(25.5)	AlCl ₃ (6.9)	3.7	EDC	Good	355
22	Low(25.5)	AlCl ₃ (6.9)	3.7	EDC	Good	642
23	High(25.0)	FeCl ₃ (15.1)	1.6	EDC	Excellent	440
24	Low(25.0)	FeCl ₃ (15.1)	1.6	EDC	Excellent	317

EDC = Ethylene Dichloride

MC = Dichloromethane

*Ratio = (mmol fiber/mmol catalyst)

** PDX = Paradichloroxylenes (3.7 mmol also present)

EXAMPLE 25

This example illustrates forming a macronet fiber from fiber which does not have active crosslinking sites, by treating the fiber with a crosslinking reagent. A 15 g sample of crosslinked fiber prepared according to Example 1 was placed in a 1 liter flask, equipped with a reflux condenser and containing 300 ml ethylene dichloride and 4.5 g paraformaldehyde. The mixture was stirred for one hour, and 50 ml of concentrated sulfuric acid was added to it. The mixture was heated to reflux temperature and refluxed overnight. The mixture was allowed to cool and the reaction was quenched by adding 100 ml deionized water. The fibers were filtered, washed twice with 100 ml deionized water and twice with 100 ml methanol, and vacuum dried overnight at 50 - 60°C.

EXAMPLES 26-32

The procedure of Example 25 was repeated using the same fibers, fibers with low crosslinking and no crosslinking, and felted and woven fibers. The fiber products of Examples 25-32 were examined for appearance and tested for surface area by BET. The results of the tests are shown in Table II.

TABLE II

Sample from Example No.	Fiber of Example No.	Polymer Crosslinking	Fiber Appearance	Surface Area by BET m ² /g
25	1-C	High	Good	215
26	1-B	Low	Good	352
27	1-C	High	Excellent	--
28	1-B	Low	Excellent	--
29	1-C	Felted	--	38
30	1-C	Woven	--	< 10
31	1-A	Uncrosslinked	--	< 10
32	1-A	Uncrosslinked	--	362

EXAMPLE 33

This example illustrates forming macronet fibers from pure polystyrene fibers. The starting fibers were highly crosslinked polystyrene with a surface area of less than one square meter per gram by BET, obtained from Engineering Yarns, Coventry, Rhode Island.

A solution of 40 ml glacial acetic acid, 2 g paraformaldehyde and 110 ml concentrated sulfuric acid was prepared in a 1 liter flask equipped with a reflux condenser. A 2 g sample of the polystyrene fiber was added, and the mixture was heated to 80°C, held at that temperature for two hours, and cooled to room temperature. A suspension of 1 g paraformaldehyde in 200 ml ethylene dichloride was added, the mixture was stirred one hour at room temperature to swell the fibers, then heated to reflux temperature and allowed to reflux overnight. The flask contents were cooled, the solvent was syphoned off, and the fibers were washed twice with 100 ml water followed by three acetone washes of 100 ml each. The washed fibers were dried under vacuum overnight at 50 - 60°C. The surface area of the fibers, measured by BET, was 23 m²/g.

EXAMPLE 34

The procedure of Example 33 was repeated. The surface area, measured by BET, of the macronet fiber from Example 34 was 40 m²/g.

EXAMPLES 35-40

These comparative examples illustrate that mere addition of a Lewis acid catalyst to swollen fibers that do not contain active crosslinking sites does not form macronet fibers. The fibers of Example 1 were swollen in either ethylene dichloride or dichloromethane, and a Lewis acid catalyst was added according to the procedure of Example 3. The mixtures were refluxed overnight, and isolated for testing according to Example 3. The fibers, catalysts and solvents for these examples are tabulated in Table III; the surface area of each material after treatment was less than 10 m²/g, indicating that no macronet structure had formed.

TABLE III

Example	Fiber Crosslinking	Catalyst	Solvent	Surface Area by BET m ² /g
35	Low	AlCl ₃	MC	< 10
36	High	AlCl ₃	MC	< 10
37	Low	SnCl ₄	EDC	< 10
38	High	SnCl ₄	EDC	< 10
39	Low	AlCl ₃	EDC	< 10
40	High	AlCl ₃	EDC	< 10

EXAMPLES 41-42

These comparative examples illustrate that reaction of chlorosulfonated fibers with a Lewis acid does not form a macronet fiber. A flask was equipped with a heater and nitrogen blanket. To this 300 ml propylene dichloride and 10 g of fiber from Example 1B (for Example 41) or ethylene dichloride and 10 g of fiber from Example 1C (for Example 42) as a swelling solvent were added. The mixture was stirred for 1 hour, and 20 g chlorosulfonic acid was added. The mixture was heated to reflux (Example 41), or to 120°C (Example 42), and maintained at that temperature overnight. The mixture was cooled, the chlorosulfonic acid was removed by suction and the chlorosulfonated fibers were washed twice with 500 ml of the same solvent in which they were swollen, and three times with 500 ml of methanol. A 5.5 ml portion of stannic chloride was added to the chlorosulfonated fibers, the mixture was heated to 80°C, maintained at that temperature overnight then isolated by washing and filtration. The fiber was dried under vacuum overnight at 50 - 60°C and was tested for surface area. Neither sample showed a significant enhancement in surface area.

EXAMPLE 43

This comparative example illustrates that amination of chlorosulfonated fibers does not form a macronet fiber. A solution of 500 ml ethylene dichloride and 6-7 g triethylenediamine was prepared in a 1 liter flask equipped with a reflux condenser. To this was added 8 g of the chlorosulfonated fibers of Example 2. The mixture was stirred for one hour, heated to reflux, and refluxed overnight. The mixture was cooled and the fibers were filtered, washed with three 300 ml portions of ethylene dichloride, and dried under vacuum overnight at 50 - 60°C. Only a small weight increase was observed, and the surface area of the fibers was not significantly increased.

EXAMPLE 44

This example shows the dynamic adsorption capacity for some of the macronet fibers from the previous examples. Dynamic adsorption capacity was measured by passing an air stream containing a known concentration of vapor through a column containing the macronet fiber adsorbent, and measuring the concentration of vapor in the effluent air stream using a gas chromatograph with an appropriate detector.

The vapor-containing stream was produced by passing a stream of dry air through a closed container containing the liquid whose vapors are to be adsorbed. The vapor concentration thus produced was determined by passing a known volume of the air-vapor mixture through a tared, activated carbon column large enough to completely adsorb all the vapor. The activated carbon column was weighed after the mixture had passed through it, to determine the total weight of vapor in the known volume of air.

The exception to the foregoing procedure for determining vapor concentration was the case of a humid vapor-air mixture of diisopropyl fluorophosphate. This air-vapor mixture was passed through a sodium hydroxide solution which scrubbed all the diisopropyl fluorophosphate from the mixture, and the total fluorophosphate concentration was calculated from the measured fluoride content of the sodium hydroxide scrubbing solution, as determined by fluoride ion electrode.

The vapors adsorbed in this example are simulants of toxic agents: dimethyl methylphosphonate (DMMP), diisopropyl fluorophosphate (DFP) and 2-chloroethyl isobutyl sulfide (CIS).

The adsorbent fibers were placed in a 3 mm diameter, glass column closed at the bottom end with a coarse sintered disk; the fiber sample was 50-100 mg, as indicated in Table IV. The air-vapor mixture was passed through the column at a flow rate of 40-75 ml/minute, equivalent to a linear flow rate of 9-17 cm/sec. The effluent from the column was split; a portion of it passed through a Hewlett-Packard Model 5880 gas chromatograph equipped with a flame ionization detector or nitrogen-phosphorus detector, as appropriate for the particular vapor, and the balance of the effluent was scrubbed through a bubble column containing 4% aqueous sodium hydroxide and was vented to a hood.

Breakthrough, defined as the time at which the concentration of the challenge vapor in the effluent stream reaches 1% of that in the influent stream, as determined from the gas chromatograph. Detector sensitivity was approximately 1 microgram/liter for DMMP and DFP, and approximately 10 micrograms/liter for CIS. The results of this example are shown in Table IV.

TABLE IV

Sample from Example No.	Sample Weight (g)	Vapor Concentration (mg/liter)	Breakthrough	
			Time (min)	Capacity (mg/g)
3	0.0603	2.23(DFP)	<3	<8.3
3*	0.0700	3.00(DFP)	<5	<16
3*	0.0781	2.01(DFP)	<3	<5.8
1-C	0.0724	2.97(DFP)	<3	<9.2
5	0.0616	2.40(DFP)	156	460
6	0.0690	2.40(DFP)	150	391
5	0.0530	2.38(DFP)	72	242
6	0.0580	2.38(DFP)	55	169
17	0.0939	1.75(DFP)	278	260
22	0.0337	1.85(DFP)	202	443
23	0.0730	1.85(DFP)	215	218
5	0.0650	2.60(DMMP)	109	327
6	0.0640	2.60(DMMP)	100	304
5	0.0509	1.53(CIS)	93	210
6	0.0469	1.53(CIS)	46	112

*Repeat preparations of Example 3.

EXAMPLES 45 - 46

These examples illustrate crosslinking swollen polymers containing active crosslinking sites; sulfuric acid is the catalyst for crosslinking. The resulting fibers contain sulfonic acid cation exchange functionality.

Five grams each of the fiber of Example 1A and 1B, chloromethylated according to the procedure of Example 2, were swollen in 300 ml of ethylene dichloride for two hours. To each fiber sample 50 ml of concentrated sulfuric acid was added, and the mixtures were heated to, and held at, the following temperatures for the following times:

40°C -	one hour
50°C -	one hour
60°C -	one hour
70°C -	one hour
85°C (reflux) -	six hours

The mixtures were cooled to about 70°C and the reaction was quenched by adding to each 125 ml of 60% aqueous sulfuric acid. The ethylene dichloride was evaporated under reduced pressure, the solutions were cooled to approximately room temperature and poured into fritted glass funnels. The treated fibers were washed three times with 250 - 300 ml of deionized water and three times with 250 - 300 ml of methanol, and were dried under vacuum overnight at 50 - 60°C. The dried fibers and untreated control fibers were tested for sulfur content, surface area by BET, and for their ability to adsorb diisopropyl fluorophosphate. Breakthrough time and capacity were determined as in Example 44. The results of these tests are shown in Table V.

TABLE V

Sample	Sulfur, %	Surface area m ² /g	Breakthrough Time (min)	Capacity (mg/g)
1A	-	5	<3	-
Example 45	5.01	58	91 ± 27	202 ± 45
1B	-	3	<3	-
Example 46	4.87	49	46 ± 7	112 ± 40

EXAMPLE 47

This example illustrates the preparation of macronet fine particles from lightly crosslinked, chloromethylated, emulsion polymerized copolymer particles.

To a 500 ml flask fitted with a mechanical stirrer, reflux condenser vented through a water scrubber, thermometer and heating mantle was charged 10.0 g of dry, chloromethylated, styrene-1.8% divinylbenzene emulsion polymer particles having an average particle diameter of about 0.1 μm and prepared according to Chong, U.S. Patent No. 4,359,537, Example 5, but dried after the initial wash and not treated with the imine or amine. To this 150 ml of technical-grade ethylene dichloride was added, and the mixture was allowed to stand overnight to swell the polymer. To the swollen polymer mixture was added 13.3 g of technical-grade aluminum chloride; the mixture was heated to reflux, and allowed to reflux overnight. The mixture was then cooled and the reaction quenched by adding, dropwise, 220 ml of acetone. The solid material was separated by filtration in a Buchner funnel; it was washed twice with acetone, twice with 3A denatured ethanol, with deionized water until the washings were neutral, and twice more with 3A denatured ethanol. The solid material was soxhlet extracted with 3A denatured ethanol for 5 hours, then dried under vacuum at 50°C overnight. The resulting macronet polymer material had a surface area (BET) of 674 m^2/g .

EXAMPLE 48

This example illustrates the preparation of macronet fine particles from lightly crosslinked, unfunctionalized, emulsion polymerized copolymer particles.

To a flask as described in Example 47 was charged 10.0 g (dry basis) of styrene-1.8% divinylbenzene emulsion polymer particles having an average particle diameter of 0.1 μm and prepared according to US-A-4,359,537, Example 1. To this 180 ml of technical-grade dichloromethane was added, and the mixture was allowed to stand for three hours to swell the polymer. To the swollen polymer mixture was added 20.0 g of technical-grade aluminum chloride; the mixture was heated to reflux and allowed to reflux for 18 hours. The mixture was then cooled and the reaction quenched by adding, dropwise, 250 ml of acetone. The solid material was separated, purified and dried according to the procedure of Example 47. The resulting macronet polymer material had a surface area (BET) of 546 m^2/g .

EXAMPLE 49

This example illustrates the preparation of macronet fine particles from lightly crosslinked, unfunctionalized, emulsion polymerized copolymer particles.

To a flask equipped as described in Example 47 was charged 10.0 g (dry basis) of styrene-0.5% divinylbenzene emulsion polymer particles having an average particle diameter of about 0.1 μm and prepared according to US-A-4,359,537, Example 1.

To this 200 ml of technical-grade dichloromethane was added and the mixture was allowed to stand overnight to swell the polymer. To the swollen polymer was added 20.0 g of technical-grade aluminum chloride; the mixture was heated to reflux and allowed to reflux for 20 hours. The mixture was then cooled and the reaction quenched by adding, dropwise, 150 ml of acetone. The solid material was separated, purified and dried according to the procedure of Example 47. The resulting macronet polymer material had a surface area (BET) of 818 m^2/g .

EXAMPLE 50

This example illustrates crosslinking of lightly crosslinked, chloromethylated, emulsion polymerized copolymer particles following a brief swelling of the particles in a solvent, to form the macronet particles of the invention.

To a 300 ml flask equipped as described in Example 47 was charged 5.0 g of the chloromethylated styrene-1.8% divinylbenzene emulsion polymer particles used in Example 47. To this 40 ml of ethylene dichloride was added. The mixture was stirred for three minutes at room temperature, then 3.9 ml stannic chloride was added in a single portion; the mixture was heated to reflux and allowed to reflux overnight. The mixture was then cooled and the reaction quenched by adding, dropwise, 30 ml of acetone. The solid material was separated, purified and dried according to the procedure of Example 47. The resulting polymer material had a surface area (BET) of 704 m^2/g and a porosity (mercury intrusion) of 1.49 ml/g .

EXAMPLE 51

This example illustrates preparation of macronet fine particles from chloromethylated, emulsion polymerized copolymer particles, and the use of these particles for adsorption of a toxic-gas simulant.

The procedure of Example 50 was followed, except that the polymer was allowed to swell overnight before the stannic chloride was added, the mixture was refluxed for 7.5 hours, and the reaction was quenched with two 50 ml portions of acetone. The mixture was allowed to stand overnight after quenching; it was then filtered in a Büchner funnel, allowed to air dry, and dried under vacuum at 50°C for three days.

The adsorption capacity of this sample, and a carbon sample of the prior art, under static conditions was determined as follows. A sample of the macronet emulsion-polymerized particles was weighed in a weighing bottle and placed in a desiccator, as was a weighed sample of BPL carbon, a coal-based activated carbon from Calgon Corporation. Dimethyl methylphosphonate was poured into the bottom of the desiccator, which was then sealed. The weighing bottles containing the macronet particle sample and the carbon sample were periodically capped, removed from the desiccator, weighed and returned to the desiccator. The weight gain from adsorption of the dimethyl methylphosphonate was reported as a weight percentage of the original sample weights, and is shown in Table VI.

Table VI

Sample	STATIC CAPACITY (WT %)				
	1 day	1 week	2 week	3 week	4 week
Ex. 51	15.1	54.4	90.7	89.3	103.1
BPL Carbon	8.9	34.7	37.8	38.6	39.0

Claims

1. A process for increasing the surface area of crosslinked poly(vinylaromatic) polymers in the form of fibers or emulsion-polymerized particles, which process comprises swelling the polymer in a swelling agent which does not deactivate Friedel-Crafts catalysts and which does not interfere with the formation of a macronet structure, and subsequently introducing additional crosslinking into the polymer to stabilize its swollen structure.

2. The process of Claim 1 wherein the polymer is a polymer of styrene, alpha-methylstyrene or styrene ring substituted by 1-3 alkyl groups of 1-3 carbon atoms each; or a copolymer thereof with less than 50% by weight of other monoethylenically unsaturated monomer.

3. The process of Claim 1 or Claim 2 wherein the polymer forms the matrix fiber of an heterogeneous polymer fiber, and wherein a plurality of fibers of polyolefin, preferably polypropylene or polybutene, are imbedded longitudinally in the matrix fiber.

4. The process of any preceding Claim wherein the swelling agent is an aromatic hydrocarbon, halogenated hydrocarbon, nitroparaffin, nitroaromatic compound, ring-halogenated aromatic compound, aliphatic hydrocarbon of six or more carbon atoms or carbon disulfide.

5. The process of any preceding Claim wherein the polymer contains active crosslinking sites, and the additional crosslinking is introduced by contacting the crosslinked polymer with a Friedel-Crafts catalyst.

6. The process of Claim 5 wherein the catalyst is ferric chloride, stannic chloride, aluminum chloride, aluminum bromide, boron trifluoride or zinc chloride.

7. The process of Claim 3 wherein the swollen polymer is allowed to react in the presence of the catalyst at a temperature from about 15°C to about 150°C for a period of from about 2 to about 24 hours.

8. The process of any of Claims 1 to 4 wherein the polymer contains no active crosslinking sites and the additional crosslinking is introduced by reacting the polymer with a crosslinking reagent.

9. The process of Claim 8 wherein the crosslinking agent is an acylating agent, preferably a diacid chloride of fumaric, maleic, malonic, succinic, adipic or sebacic acid, phosgene or thiophosgene; or an alkylating agent, preferably methyl halomethyl ether, alpha, alpha-dichloro-p-xylene, dichloromethane, bis (4,4'-chloromethyl) biphenyl, bis(chloromethyl) thiophene, 4-dichlorohexane, 1,4-dichlorobutane, chloroform, carbon tetrachloride, an alkylene glycol, a diepoxide, a polybutadiene, paraformaldehyde in the presence of a strong acid, formaldehyde in the presence of a strong acid, or a formaldehyde generator in the presence of a strong acid.

10. The process of Claim 8 or Claim 9 wherein the swollen polymer is reacted with the crosslinking reagent at a temperature from about 15° to about 150°C for a period of from about 2 to about 24 hours.

11. A crosslinked poly(vinylaromatic) polymer, in the form of a fiber or an emulsion polymerized particle, having a macronet structure and a surface area of at least 100 m²/g.

12. The polymer of Claim 11, being a polymer of styrene, alpha-methylstyrene or styrene ring substituted by 1-3 alkyl groups of 1-3 carbon atoms each; or a copolymer thereof with less than 50% by weight of other monethylenically unsaturated monomer.

13. The polymer of Claim 11 or Claim 12 wherein the polymer forms the matrix fiber of an heterogeneous

polymer fiber and wherein a plurality of fibers of polyolefin, preferably polypropylene or polybutene, are imbedded longitudinally in the matrix fiber.

14. The polymer of any of Claims 11 to 13, chemically functionalized for adsorptive, organic-reactive or ion exchange functionality.

15. The use of a polymer of any of Claims 11 to 14 as an adsorbent or ion exchange material.

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Operations Patent Department Lennig House
2 Mason's Avenue
Croydon CR9 3NB(GB)(54) **High-surface-area compositions.**

(57) Polyaromatic fibers or microbeads which are swollen with solvent and crosslinked while swollen in such a way that the expanded, or macronet, structure of the swollen fiber or microbead is stabilized and retained even after drying, exhibit high surface area and significant adsorptive capacity.

EP 0 314 449 A3



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EUROPEAN SEARCH REPORT

Application Number

EP 88 31 0053

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 152 780 (MITSUBISHI CHEMICAL INDUSTRIES) * Claims 1-7; pages 6-9 * & US-A-4 543 365 (Cat. D,Y) -----	1,2,4-12, 14,15	C 08 F 8/00 C 08 J 3/00
Y	EP-A-0 007 791 (ROHM AND HAAS) * Claims 1-17; pages 18-21 * -----	1,2,4-12, 14,15	
Y	EP-A-0 007 792 (ROHM AND HAAS) * Claims 1-11 * & US-A-4 263 407 (Cat. D,Y) -----	1,2,4-12, 14,15	
A	CHEMICAL ABSTRACTS, vol. 100, no. 24, June 1984, page 21, abstract no. 192592x, Columbus, Ohio, US; & CS-A-215 801 (J. KAHOVEC) 20-12-1983 * Abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 F C 08 J
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		26 June 91	PERMENTIER W.A.
<div>CATEGORY OF CITED DOCUMENTS</div> <div><div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div><div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document</div></div>			